

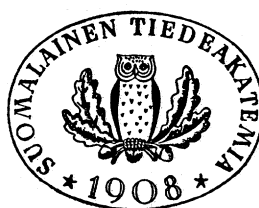
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A STUDY OF GAS-LIQUID MULTIPLE
DISTRIBUTION WITH MIXING
OF THE LIQUID PHASE



HELSINKI 1963
SUOMALAINEN TIEDEAKATEMIA

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PREFACE

The present work was carried out in the Laboratory of the Foundation for Chemical Research, Biochemical Institute, Helsinki, during the years 1961—1963. Some of the results were published as a preliminary report in 1961.

Professor Artturi I. Virtanen, Director of the Biochemical Institute, has given me guidance and advice without stinting his time, and placed all the necessary laboratory facilities at my disposal, throughout the course of this investigation. I wish to express my sincere gratitude to him for all this.

My gratitude is also due to my colleagues at the Biochemical Institute, who have been helpful to me in many ways.

The work was facilitated by the skilled technical assistance of Miss Leena Puolitaival, Miss Synnöve Rinne, Mr. K. Järvinen, and Mr. J. Valtonen. I wish to thank them for this help.

I also wish to extend my thanks to Mrs. Jean Margaret Perttunen, B.Sc., for her valuable assistance in revising the English of my manuscript.

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Helsinki, April 1963.

ÖRN WAHLROOS

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INTRODUCTION

Almost all chemical work involves some kind of analysis. A choice may be made between analyses based on the physical properties of the material, on separation of its components, and on a combination of these two methods. Because of the lack of specificity of many physical methods, or because the number of variables involved tends to become inconveniently large when several compounds are mixed, separation is usually necessary. An alternative is to collect many physical data concerning a mixture and solve the equation system thus obtained. This method is time-consuming unless a computing machine is available and has not gained popularity except in mass and optical spectrometric work. Thus the development of the theory of counter-current or multistage systems, which began with the classical work of Martin⁶⁷, van Deemter¹⁷, and Craig¹², to mention only a few names, and has led to effective separation methods, may be regarded as one of the greatest achievements of analytical chemistry.

Multistage separation in liquid-liquid systems had been in use²⁴ before it was realized that the plate height could be reduced and the number of stages thus increased⁶⁷ by the use of a solid support for one of the phases. This chromatographic method was then directly applied to the gas-liquid system. Historically, the investigation of a multistage gas-liquid system represents a step backwards. In preparative work, however, a large effective plate volume is needed. Because this seemed to be more easily established in a multistage apparatus, and because the behaviour of such an apparatus is easier to predict, the performance of a multistage gas-liquid distribution apparatus was investigated.

REVIEW OF THE LITERATURE

With complex samples, some kind of prefractionation or cleaning-up procedure⁵⁸ is usually necessary prior to the use of more refined chromatographic methods. Interest has been concentrated on the development of the latter, and preparative procedures have mainly been developed in connexion with industrial processes.

A situation often encountered with samples of biological origin is the need to detect or separate trace components in the presence of a large amount of a substance of about the same volatility (water). On an analytical column, this main component, by saturating part of the column, may mask some of the trace substances, however sensitive the detector is. Thus, for both detection and isolation the apparatus should be capable of functioning over a wide range of sample sizes⁵⁰. Other desirable features are applicability to a wide range of compounds, efficiency, predictable behaviour, and simplicity. It may be desirable to compare different fractionation methods as to the extent they are meeting these demands. Absorption, with formation of non-volatile derivatives, and adsorption¹⁹ will be omitted from the present consideration, because of the possibility of irreversible changes, and because of compound specificity.

1. Distillation

Distillation, which, together with vacuum manipulation, absorption and adsorption, was the only method for the fractionation of volatile mixtures before the introduction of chromatography, has been developed to a technique of considerable subtlety. Laboratory columns, two metres high, with an efficiency of one theoretical plate per centimetre, have been built⁵². The focus of interest is now a better understanding of the dynamic characteristics of columns²³.

In spite of the high resolving power of gas chromatography, distillation is often preferred because of the large throughput of material possible. More specific methods than normal distillation, in which separation depends on the volatility ratio (α) of the components,

$$\alpha = \frac{p_{01} \cdot \gamma_1}{p_{02} \cdot \gamma_2}$$

(p_{01} = vapour pressure of pure component 1, p_{02} = vapour pressure of pure component 2, γ_1 = activity coefficient of component 1, γ_2 = activity coefficient of component 2) are the azeotropic method, in which a substance is added, giving a volatility ratio $\alpha = 1$ for one concentration with one component, and extractive distillation, in which an additional substance is introduced to bring about such a change in the activity coefficients of the compounds that⁸²

$$|\log \alpha_e| > |\log \alpha|; \alpha_e \neq 1$$

Whilst normal distillation is limited to compounds boiling at temperatures about 10 degrees apart and azeotropic distillation is hampered by the difficulty of separating the material from its azeotropic mixture⁸², extractive

distillation remains a method which can compete with gas chromatography in separating power and general applicability on a laboratory scale. In fact, great similarity exists between gas chromatography and extractive distillation^{81, 96}.

Steel-spiral-filled columns⁸² and spinning-band columns⁵² have shown the highest efficiency, the plate efficiency of practical plate columns usually being less than 1⁸². Kuhn⁶² developed an expression for the relation between the plate height in packed columns and the mass transfer rate (term A) in the gas phase, the mass transfer resistance in the liquid phase (B), and the longitudinal diffusion (C) in the column.

$$HETP = \frac{11}{48} \cdot \frac{a_D^2 \cdot H_D}{D_D} + \frac{33}{140} \cdot \frac{d_L^2 \cdot H_H}{D_L} + \frac{D_D}{H_D}$$

$$(H = \quad A \quad + \quad B \quad + \quad C)$$

(a_D = thickness of the vapour layer, d_L = thickness of the liquid layer, D_D = diffusion coefficient vapour, D_L = diffusion coefficient liquid, H_D = average vapour flow rate, H_H = load = vapour velocity in moles \cdot sec⁻¹ \cdot (area of cross-section of the tube)⁻¹).

Because of the rather slow mass transfer in a column, diffusion in the transverse direction will be small. Any asymmetry in packing or liquid flow will thus tend to broaden the theoretical plate height. Therefore the packing should be even and provide a large area for vapour-liquid exchange. In addition the liquid flow (whether of reflux or extracting liquid) should be carefully controlled, and the liquid should have a low viscosity. In spinning-band columns, mass exchange is accelerated by means of mechanical mixing. The difficulties involved in controlling flow and/or slow mass transfer are probably responsible for the lower efficiency (practical plate efficiency 35 to 48%) when bubble-cap tray columns (normal practical plate efficiency 80%) are used for extractive distillation^{28, 59}. The fact, observed by Röck⁸², that the plate number of a column does not increase in proportion to its length is probably due to slight asymmetries in the column (canal formation, temperature fluctuations). To overcome this difficulty, Röck suggested the use of several columns connected by mixing tubes. A further complication is that the separation factor α_e is dependent on the concentration of the extracting liquid, and may impede the plate height if fluctuations in the flow rate occur⁸².

Usually the separation factor α is lower at higher temperatures, because deviations from ideality become smaller and the ratio between the activity coefficients approaches one. Another reason for keeping the temperature low, especially with biological materials, is that the risk for artefact formation increases with temperature^{69, 97}. For any given plate number, it

would therefore be of advantage to work at lower pressures. At reduced pressures, however, packed columns are not useful because of their high pressure resistance⁸². Zuiderweg⁹⁹, as well as Nerheim and Dinerstein⁷¹, found that the efficiency of the spinning-band columns diminished with reduction in pressure (by about 30% on going from 760 to 300 torr). This might be explained by supposing that the greater diffusivity in the gas phase leads to longitudinal spreading.

The effect of column hold-up on plate height has been studied by Zuiderweg⁹⁹. Efficiency reaches a maximum at a hold-up volume of 30 to 50% of the charge volume. When the hold-up increases beyond this value, its influence becomes of little importance. If the hold-up is 100% or higher, separation is poor and cannot be improved by increasing the plate number or the reflux ratio.

When the concentration of the product is calculated⁸², it is usually assumed that α is constant, that the hold-up of the column is negligible as compared with the charge, and that it does not influence the *HETP* of the column. In calculating the plate number needed, account is taken of the effect of the reflux ratio, which is comparable to the recycling method in chromatography⁶⁶, in which all the plates are used. At a given α , a minimum reflux ratio may be calculated, where separation is possible only at an infinite number of plates. At total reflux, a minimum number of plates are needed. From this it follows that at low α values a high reflux ratio has to be used. The high reflux is difficult to control and results in slow distillation. A usual arrangement is a two-metre column with 200 theoretical plates operated at a reflux ratio of 100 to 200, and giving 30 cm³ of distillate per hour⁸². As was found by Zuiderweg⁹⁹, a very pure distillate cannot be obtained at low starting concentrations when finite reflux ratios are used, however large the plate number is. An attempt to circumvent the difficulties due to large hold-up volume by blowing an inert gas through the column was made by Huppes⁴⁴. Apart from bringing about some improvement in the separation of components present in low concentrations, the introduction of the gas had the added advantage of facilitating heating control, and lowering the operating temperature.

In the methods of column testing, the plate number is determined at total reflux. However, during the actual operation the plate number is different; it is often somewhat higher at low reflux because of the thinner liquid layer⁸². The many variables make it difficult to calculate the plate number of a column when a change in the system is made. Hence the column should be tested for each system used.

Vacuum manipulation of volatile compounds has been employed by Niegisch and Stahl⁷² for prefractionation of biological material prior to gas chromatography. The method⁸³, which depends on the rapid diffusion of

vapour at a pressure of 10 microns or less and their condensation at different temperatures, has the advantage that small samples can be handled without losses. Separation is poor, however, and an apparatus for multiplication of the single diffusion-condensation effect would be rather complicated. The time allowed for diffusion is important for separation; at equilibrium all condensable material is at the point with the lowest temperature.

Condensation in low-temperature traps through which carrier gas is flowing is in principle applicable only to concentrated mixtures. The losses, which should theoretically be equal to the product of the vapour pressure at the temperature of the trap, the volume of carrier gas passing through, and $1/R$, are usually larger on account of aerosol formation⁷⁹.

Among the industrial methods, thermal diffusion may be used for the concentration of trace components, but is restricted to thermally stable substances. Considerable interest attaches to the methods for gas separation by absorption in liquids, such as the absorption tower process for corrosive gases, and the pressure-gradient separation of low-boiling mixtures¹³. These could be used systematically in a multiple way. It should also be observed that the fractionation of volatile compounds in liquid-liquid systems⁴² is sometimes superior to gas-liquid systems, because the greater deviations from ideality produce greater differences in the partition coefficients in such systems.

2. Preparative gas chromatography

In gas-liquid chromatography, as in extractive distillation, separation depends on the relative volatility of the components. The former process differs from the latter in that only the part of the column occupied by the bands is utilized. On the other hand, large numbers of plates are more easily achieved with analytical columns¹⁷.

The maximum sample size on a packed chromatographic column, if excessive broadening of the bands is to be avoided, is given by Keulemans^{54, 60} as

$$0.5 \sqrt{n} \cdot (V'_g + kV'_L)$$

(n = number of plates, V'_g = gas volume of the plate, V'_L = liquid volume, and k = distribution coefficient). The formula expresses the fact that the columns can be scaled up by an increase in the plate number (because the broadening of the peaks is proportional to \sqrt{n} . At a high value of n , when only the first plate or plates are saturated at injection, the difference in band width is small⁷⁸), and/or in the effective plate volume. Here, the

liquid volume of the plate and the partition coefficient are the factors to be increased.

The method usually chosen to achieve this is to increase the whole plate volume by the use of wide diameter columns, in which the increase in the liquid volume is relatively greater (up to 40% by weight of the filling material). Standard analytical columns, 4 mm in diameter, with about 20% liquid phase and about 2000 plates may be loaded with 10 mg of sample⁴⁶. If some spreading of the peaks is allowed, a 10 cm diameter column with 500 plates may be loaded with 50 g of mixture, under the same conditions⁵⁻⁷. On the other hand, Ackman *et al.*¹ report that a column 1.8 cm in diameter and 8 m long was grossly overloaded with samples of 1 g or more.

The broadening of the *HETP* with increasing amounts of the stationary phase has been studied by Keulemans and Kwantes⁵⁵. The increase is governed by the slow rate of diffusion in the liquid phase. The minimum of the *HETP* gas velocity curve is sharper at high concentrations, making maintenance of low pressure gradients along the column more important. The main problems of upscaling, however, are the difficulties of obtaining uniform introduction of the sample and uniform flow patterns. The first problem has been tackled by the complete vaporization of the samples with special vaporizers^{3, 5-7}. The more serious problem, however, is to obtain uniform column packings, which will determine the flow pattern. The increase of the *HETP* with column diameter has been studied by Bayer *et al.*⁵⁻⁷ and Huyten *et al.*⁴⁵. The latter authors showed that in a large-diameter column, partly owing to a wall effect and partly owing to the mode of packing, the velocity differences were pronounced and gave rise to radially symmetrical velocity profiles. This effect was counteracted by radial diffusion, which also depends on the mode of packing. The theoretical plate height was expressed by adding a term (*D*) to the van Deemter expression^{17, 45}

$$HETP = A + B/U' + CU' + DU'$$

(*A* = «eddy diffusion» term, *B* = molecular diffusion term, *C* = resistance to mass transfer in the liquid phase, *U'* = gas velocity.)

The *D* term is proportional to the square of the column radius and to the reciprocal of the effective radial diffusion coefficient, which is small for dense packings. Experimentally, van Huyten *et al.*⁴⁵ found radial diffusion to be complete for a 1 m column length when the diameter was 7.5 cm. They were also able to increase efficiency by dividing the column into 1 m pieces, connected by empty tubes, so that the components could be mixed at intervals. By theoretical evaluation of the effect of asymmetry across the column diameter, Golay³⁶ arrived at the conclusion that the increase in plate height due to the wall effect is independent of the column radius when

this is much larger than the diameter of the packing particles, and that the optimum length of the column between the mixing tubes is proportional to the gas velocity, the square of the mixing tube diameter, and the reciprocals of the gas diffusion and asymmetry coefficients. Application of the latter expression to the experimental values of Huyten *et al.* leads to a reasonably good correlation. The larger values of the wall effect found by Huyten *et al.*⁴⁵ probably depend on the mode of packing, there being a radial packing density gradient. Attempts to eliminate the wall effect have been made by insertion of impregnated washers at intervals in the packing²⁶; however, conflicting results have been obtained with this method⁹². Different modes of packing have been studied by Pypker⁷⁶, and by Giddings and Fuller³³.

The throughput of material may also be increased by the use of narrow, matched columns in parallel⁴⁸, by automatic, repetitive running on one narrow column³, or by continuous methods. Among the latter, the true countercurrent method devised by Schulz⁸⁶ which somewhat resembles the O'Keeffe distribution in liquid-liquid systems⁴¹, has found industrial applications. In the system of Thompson⁹⁰ the continuous feed is made in the form of a concentration wave, which is resolved in a cascade of short columns to avoid the high pressure drop in longer columns. Interesting proposals for a continuous system with the gas and liquid phases moving at right angles to each other, have been made by Giddings³¹ and by Turina *et al.*⁹¹. In the method of the latter authors no solid support is used.

Because the optimum carrier gas velocity increases proportionally to the cross-section area of the column, and the sample, when eluted⁵⁴, is diluted in proportion to the effective plate volume, difficulties are encountered in the quantitative collection of the eluted components¹. The yield for large samples can be increased to 98% with special equipment^{6, 21, 49, 80, 89}, but condensation of trace components may be impossible to achieve.

Methods more suited in principle for the preparative separation of samples with great concentration differences are programmed temperature chromatography³⁸, and chromatothermography^{70, 98}, in which the dilution is reduced by a continuous reduction of the k -values during the elution process. With the latter method, an exponential increase of the concentration in a band can be obtained with a temperature gradient in the longitudinal direction of the column. This is counteracted by the nullifying effect of steep gradients on separation. A practical limit to the full exploitation of these methods is set by the low heat conductivity of the packing materials. This leads to a paraboloid temperature distribution across the tube⁷⁷ and thus increases the wall effect present in isothermal columns.

EXPERIMENTAL

1. Distribution apparatus

The distribution apparatus^{93, 94} used consists simply of gas washing bottles (Fig. 1) connected in series with Teflon tubing of 2 mm inner diameter, and a means for effectively mixing their liquid content.

In all instances the outer dimensions of the washing tubes were the same, inner $\varnothing = 1.2$ cm, length 11 cm, wall thickness about 1.5 mm. The inner tube diameters were 0.4/0.7, 2/4, 4/6 and 8/10 mm. In the first case, the inner tube consisted of a steel capillary, silver soldered to a screw lid fitting on the tube. Unless otherwise stated, the experimental results were obtained with inner tubes of 2 mm diameter. The simple Teflon tubing-to-glass seal was found to withstand pressures up to at least 2.5 atmospheres of nitrogen at room temperature. Above 150°C the tubing has to be secured with wire or a spring because of the softening of the Teflon wall. For the experiments with the gas as the moving phase, the gas flow was maintained by adjustment of the inlet pressure with a conventional membrane valve. For the experiments with the liquid as the mobile phase, an improvised liquid pump was used. The gas flow rate was determined with a soap-film meter.

The glass tubes are attached to a steel rod ($\varnothing = 6.6$ mm) by means of spiral springs made of 0.6 mm steel thread. The force constant of each spring

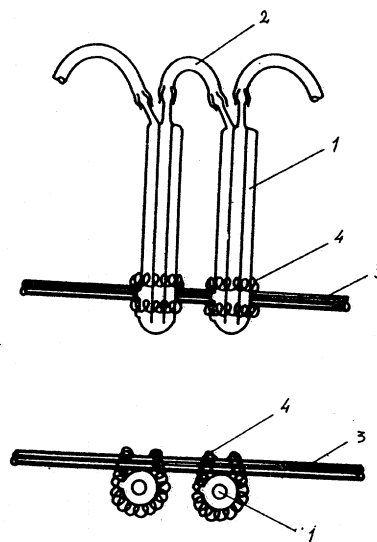


Fig. 1 a. Side view of a section of the distribution apparatus.
b. Top view of the same section.
1. Glass tube. 2. Teflon tubing. 3. Steel rod. 4. Steel spiral spring.

is about 460 Newtons/m. The tubes are attached 5 cm below their centre of gravity. On a 2 m rod 100 tubes, each weighing about 19 g, can be attached. One end of the steel rod is connected to an electromagnetic vibrator (type «Vibromix», 40 W, frequency 100 c/sec), so that the rod oscillates in the longitudinal plane. The rod is supported at 70 cm intervals by Teflon bearings. When the liquid content of each tube is between 0 and 5 cm³, the tubes' individual frequency is sufficiently near to that of the vibrator for resonance to occur between the tubes and the vibrating rod, and the tube contents are efficiently mixed. No very clear internodes were observed; on vibrating, the tubes settled at somewhat different levels. With prolonged vibration, steel capillaries may be broken by fatigue but the Teflon tubing withstands the vibration.

2. Measurement of the amplitude of vibration of the tubes and the viscosity of the liquid phases

The amplitude of vibration was varied by adjusting the voltage of the vibrator with a variable transformer. The amplitude of the rod and the tubes at various voltages was measured with a differential transformer coupled to an oscilloscope via a 1:34 step-up transformer. The «home-made» differential transformer had a core weighing 0.569 g and was fed with 1000 cps alternating voltage. The vibration amplitude of the tubes (Fig. 2) was obtained

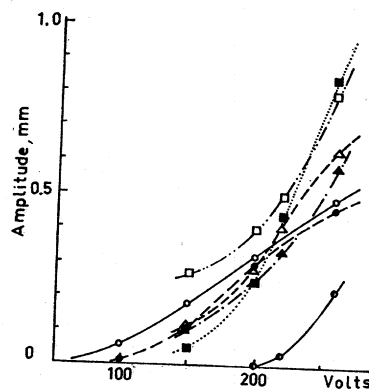


Fig. 2. Ordinate: amplitude in mm. Abcissa: voltage fed to the «Vibromixer».

- Longitudinal amplitude of the steel rod.
- » » » tube, 6 cm above the rod.
- C— Amplitude at right angles to the tube-rod plane, 0.5 cm from bottom of tube, $V_L = 0.5 \text{ cm}^3$
- △— Longitudinal amplitude of tube, 0.5 cm from bottom; 0.5 cm³ cineole/tube
- ▲— As above, but 2 cm³ cineole/tube
- » » » 4 » »
- » » » 6 » »

from the modulation amplitude of the alternating voltage visible on the oscilloscope screen. The response was linear over the range measured. The drift of the 1000 cps oscillator was taken into account by measuring the maximum signal before and after the measurement. The load was 20 tubes.

At a load of 60 tubes, the amplitude at 260 V is only 0.1 mm, because the greater friction and the increase in mass results in a lower individual frequency, so that a higher energy input to the vibrator is required to maintain the amplitude at the same value.

At room temperature and a gas flow rate of 100 cm³ N₂/min, the pressure drop for 10 tubes, each containing 1 cm³ of cineole, was 18 cm of water at an amplitude of 0.1 mm and 15.7 cm at 0.7 mm.

The viscosity of the solvents used (Table 1) was partly determined by the Ostwald method, partly obtained from the Handbook of Chemistry and Physics⁴³. As the distribution experiments were performed at room temperature, the change of viscosity between 19°C and 25°C was estimated, and the temperature during the various runs recorded.

Table 1

Solvents used in distribution experiments.

Solvent	Viscosity CP, at +20°C	Solvent	Viscosity CP, at +20°C
<i>n</i> -Heptane (Fluka)	0.4	Paraffin oil	168
«High Flash white spirits» (Shell)	1.1	Quinoline	4.9
«Shell Sol T» (Shell)	1.5	40% isopropanol in water	2.9
<i>n</i> -Hexadecane (BDH)	3.4	8% starch in water	4.9
Cineole (Fluka)	4.6	Water	1.0
Squalane (BDH)	33		

3. Samples

In the majority of the distributions, the sample was a hydrocarbon mixture. Its qualitative composition (Fig. 3) was determined by gas chromatography, using a 1.8 m column of tritolyl phosphate (10%) + H₃PO₄ (2%) on 40 to 60 M firebrick, a 1.8 m column of dinonyl phthalate (DNP) (10%) on 40 to 60 M firebrick, and a 1 m column of 1% methyl cellosolve, saturated with silver nitrate at room temperature on 80 to 100 M Celite, in series. The column diameter was 5 mm, the argon flow rate at the outlet was 65 cm³/min, and the experiment was conducted at room temperature.

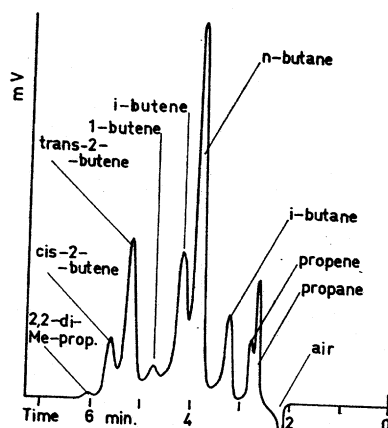


Fig. 3. Gas chromatogram of the hydrocarbon mixture used as a sample. For conditions see text.

A β -ray argon tetrode, developed in connection with this work, was used as a detector⁹⁵. It was operated at 600 V. The peaks were identified by means of the subtraction method⁴, using concentrated sulphuric acid for absorption of olefines, the retention data given by Scholly *et al.*⁸⁴ and Smith *et al.*⁸⁸, and the retention data obtained during the distribution experiments on nonpolar solvents, in combination with the boiling points⁴³. Gaseous samples were injected into the first tube through the tubing connecting it to the carrier gas cylinder. Liquid samples were injected in the same way, in liquid form.

4. Detection of solute bands. Calculation of *HETP* and *k*

During most of the determinations of *HETP* as a function of various parameters, the load of the apparatus was 12 tubes.

The form and position of the distribution curves were determined by withdrawing a sample of known volume of either the liquid or the gas phase of each tube with a syringe and directly injecting it into the gas chromatographic system described above. For higher-boiling samples a 1.8 m DNP column at elevated temperature was used for analysis. Usually the gas stream was stopped before any component was eluted. The peak heights were taken as a measure of the relative concentration. A few parallel determinations with elution of the sample and detection with a catharometer of conventional design connected to the distribution apparatus gave the same results regarding the band shape, *HETP*, and distribution coefficient

The number of theoretical plates per tube (n/tu) in the distribution which is of the expected Poisson type⁵⁴ (Fig. 4), was calculated according to the plate theory⁵⁴ from the width (W_t) of the curve, defined as the distance (in number of tubes) between the intersections of the tangents with the tube-number axis, and the number of the median tube (p_t)

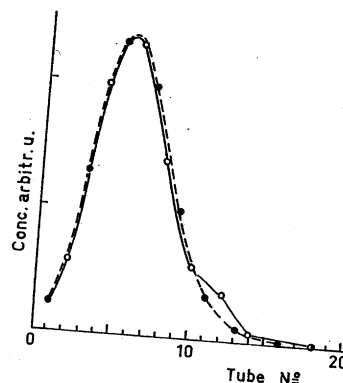


Fig. 4. Solid line: experimental distribution curve. Broken line: calculated Poisson distribution⁵⁴. The concentration is expressed in arbitrary units. Solute benzene, solvent cineole, $V_L = 2 \text{ cm}^3$.

$$(1) \quad \frac{n}{tu} = \frac{16 \cdot p_t}{W_t^2}$$

derived by insertion of the values $w = (n/tu) \cdot W_t$ and $n_t = (n/tu) \cdot p_t$ in $w = 4 \cdot \sqrt{n_t}$. The theoretical plate height (H) will here be defined as the part of one tube containing one plate:

$$(2) \quad H = \frac{tu}{n}$$

The distribution coefficients (k) were calculated according to basic theory from equation (3)⁵⁴

$$(3) \quad V_R = p_t (V_g + k V_L)$$

(V_R = retention volume, V_g = gas volume/tube, V_L = liquid volume/tube).

The standard deviation for the n/tu values for seven parallel determinations was 0.22, for the distribution coefficient of propane, $k_{av} = 14.7$ on Shell Sol T, the S. D. was 2.1 as calculated from eleven determinations.

5. Method for the rapid estimation of distribution coefficients

a. Method

The method developed⁹³ is based on logarithmic dilution, a principle which has been used by Lovelock⁶⁴ for the calibration of gas chromatographic detectors. Because two additional variables are involved and because the formula for detector calibrators has been published in a somewhat erroneous form in the literature^{56, 64, 65} the derivation of the formula for the distribution coefficient will be given here.

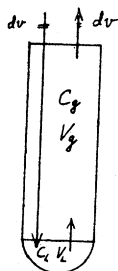


Fig. 5. Schematic representation of the mixing vessel for the determination of distribution coefficients.

Consider a vessel containing a gas volume V_g and a liquid volume V_L of low volatility (Fig. 5). Gas is blown through the vessel at the rate $U = dv/dt$. At time t_0 W moles or grams of a volatile sample are introduced. Both gas and liquid phases are mixed to achieve rapid equilibration of vapour between gas and liquid leading to the concentrations C_g and C_L .

Mass balance requires that

$$-C_g dv = V_L dC_L + V_g dC_g$$

Elimination of C_L by the relation⁵⁴

$$(4) \quad C_L = kC_g$$

gives

$$\frac{dC_g}{C_g} = - \frac{1}{V_g + kV_L} dv = - \frac{U}{V_g + kV_L} dt$$

and by integration and putting $C_g = C_{g_0}$ at time $t = 0$

$$(5) \quad \ln C_g = \ln C_{g_0} - \frac{U \cdot t}{V_g + kV_L}$$

or

$$(6) \quad \ln \left(\frac{W}{V_g + kV_L} \right) = \ln \left(\frac{W_0}{V_g + kV_L} \right) - \frac{U \cdot t}{V_g + kV_L}$$

From (5) it is seen that provided mixing is adequate and the detector shows a linear response over the concentration range, a plot of log (detector signal) against time should be a straight line with the slope $-U/V_g + kV_L$, intercepting the log concentration axis at the starting concentration, if the distribution coefficient is independent of concentration over the range measured. In Fig. 6 a and 6 b the recorder trace and its logarithmic plot are

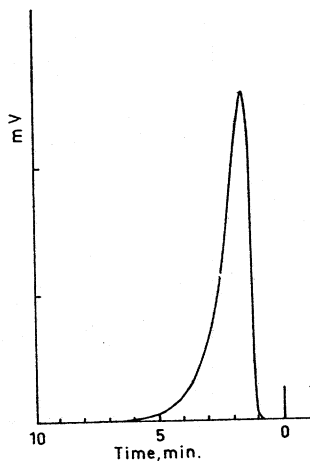


Fig. 6 a. Recorder trace obtained at determination of the distribution coefficient of cyclohexane (10 μ l) between nitrogen and quinoline. $V_L = 0.25$ cm³, $U = 105$ cm³/min, $t = 23^\circ\text{C}$, $V_{\text{eff.}} = 20$ cm³, $k_{\text{det.}} = 274$.

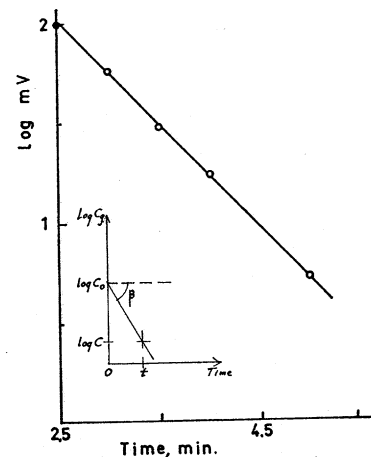


Fig. 6 b. Log-linear plot of the descending part of the curve from Fig. 6 a.

shown for cyclohexane on quinoline. Here, one of the tubes shown in Fig. 1, connected to a vibrator, was used as the mixing vessel. Instead of providing the vessel with an additional mixer for the gas phase, the signal obtained on injecting benzene vapour into the empty tube ($V_L = 0$) was used for calculating the «effective volume» from (5) for the tube, and this value was used instead of V_g in the formula

$$k = - (U + 2.3 \cdot V_g \cdot tg\beta) / (2.3 \cdot V_L \cdot tg\beta)$$

The carrier gas (N_2) velocity through the mixing tube was measured with a soap-film meter. A continuous sample from the gas stream issuing from the tube was withdrawn by means of a gas injection pump⁶⁵ connected to an argon tetrode detector. The use of the «effective volume» should also com-

pensate for adsorption effects in the tubing and broadening in the injection pump leading to the detector. The »effective volume» should be determined for the carrier gas velocity and compounds used, and the argon velocity in the injection pump should be carefully controlled. The performance of the apparatus might be improved by the addition of a mixer for the gas phase (for example, a vibrating reed and a magnet), a flame ionization detector (which has a wide linear range), a log-linear recorder, and thermostating.

b. Discussion

The method provides data on k over a considerable concentration range in one experiment. The concentration limit is set by the detector sensitivity. On the other hand, with high values of k , the duration of one determination may be short, unless a wide range scan is wanted, as only the slope is required. If the k 's of two components differ by a factor of at least two, the k 's may be determined from the mixture in one experiment (Fig. 7) (as in the analysis of a decay curve of two radioactive nuclides). In Table 2 distribution coefficients estimated in this way are listed together with some values obtained on multiple distribution (eq. 3).

The static methods^{10, 25, 47, 85} for measuring the distribution coefficients are accurate (Brewer *et al.*¹⁰ report an experimental precision of 0.1%) but time-consuming, allowing 2 to 3 determinations per 24 h. Gas chromatography has been used for the determination of distribution coefficients,

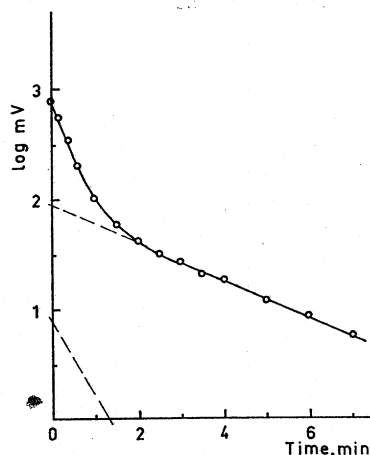


Fig. 7. Simultaneous determination of the distribution coefficients of ether and cyclohexane between cineole and nitrogen. 10 μ l mixture 4:1 (v/v) injected. Solid line: log signal. Broken lines: construction of the slope due to ether. $V_L = 0.25$ cm³, $V_g = 14$ cm³, $U = 107$ cm³/min, $t = 22.7^\circ\text{C}$, k (cyclohexane) = 850, k (ether) = 213.

Table 2

Estimations of distribution coefficients by the method of logarithmic dilution.

Sample	Liquid phase	t°C	k	Values by multiple distribution
Benzene	Cineole	23	1340	$k = 1150$
»	»	22	1005	
»	»	18	1420	
»	»	»	1253	
Cyclohexane	»	»	822	$k = 900$
»	»	»	822	
»	»	»	865	
Ether + Cyclohexane	»	»	$k_e = 213, k_c = 850$	
— » —	»	»	$k_e = 240, k_c = 845$	
Benzene	Quinoline	»	1230	
»	»	»	1280	
»	»	23	1090	
»	»	»	1110	
Cyclohexane	»	»	238	
»	»	»	294	
»	»	»	270	
»	»	»	274	
Benzene + Cyclohexane	»	»	$k_B = 1000, k_c = 310$	$k_B/k_c = 3.0;$ $\left(\frac{1000}{310} = 3.22\right)$
Ether	Water	17	21	$k = 22$
»	»	»	23	
»	»	22	14	

both in a search for a suitable solvent in chromatography and extractive distillation, and in theoretical work^{14, 18, 40, 63}. A new column is made for every liquid phase tested. In a review by Habgood³⁹ it is pointed out that the use of gas chromatography for this purpose is open to some criticism, partly because of the effect of non-linearity on the peak shape (corrections for this have been worked out by Cremer *et al.*¹⁵, partly because the liquids used in gas-liquid chromatography are substances with extreme properties, but mainly because the liquids are dispersed on solids whose properties are not always fully known. Thus, in addition to solubility, the distribution may involve adsorption at the gas-liquid interface⁶⁸ and at the liquid-solid interface⁵³. The two latter factors may be negligible in normal cases, *i.e.*, when the amounts of liquid on the support are not too small. Everett and Stoddart²², working with hydrocarbons, found close agreement with values obtained by conventional methods. Even with supports treated with in-

activators and liquid amounting to 20%, adsorption is sometimes observed with polar solutes, however. This corroborates the results of Giddings³², who has shown that the stationary phase, rather than spreading into an even layer, forms droplets in the pores of the support thus leaving part of the solid surface free. Funk *et al.*²⁷, on the other hand, showed that excessively thick liquid layers may be unable to equilibrate fully with the gas phase. Keller *et al.*⁵³ developed an expression for the relative contributions made by adsorption and by solution to the distribution coefficients; a practical difficulty is that the adsorptive properties of the uncoated support are not necessarily the same as those of the coated support. In the method described above this difficulty should be obviated, because a large proportion of liquid can be used relative to the adsorptive surface (the walls of the vessel). The mixing efficiency is such that equilibrium is attained with gas velocities up to 600 cm³/min when the viscosity of the liquid is 4.9 CP. Higher viscosities require lower gas velocities ($U = 50$ cm³/min at $\eta = 160$ CP).

RESULTS

I. GAS AS THE MOVING PHASE

1. Working range for tube efficiency ≥ 1

Because the linear gas velocity in the capillaries is larger than the velocity in the tubes, at low pressures $U_k/U_t = \phi_i/\phi_k$, back diffusion in the gas phase is low, while sufficient time is allowed for equilibration between the gas and the liquid in the tube. With an inner tube ϕ of 0.04 cm, the minimum gas flow rate with nitrogen was found to be less than 3 cm³/min with cineole as the solvent ($\eta = 4.34$), and ether as the sample, at room temperature. With an inner tube $\phi_k = 0.2$ cm, the efficiency fell below 1 plate/tube at the velocity 7 cm³ N₂/min, corresponding to about 14 times the rate of diffusion calculated from the published values of the diffusion coefficients. Here, according to the van Deemter equation, the contribution of gaseous diffusion, $2 D_g/U'$, to the plate height would be 0.5 mm, or about 0.5% of the length of one tube.

The upper limit for the gas velocity depends on the time (t_e) required for one equilibration. Because the ratio of gaseous diffusion to liquid diffusion constants is of the order of 10^4 , the rate-limiting step in the equilibration will be the mass transfer in the liquid phase. The time required for a molecule to diffuse the distance d_L is equal to $d_L^2/2n'D_L$, where n' is the number of directions and D_L the diffusion constant⁵¹. Thus, the mixing efficiency may be characterized in terms of the inverse value of the ratio

$$(7) \quad t_e = \frac{d_L'^2}{2 \cdot 3 \cdot D_L'}$$

where d_L' = the effective liquid layer thickness and D_L' = the effective »liquid diffusion coefficient«. D_L' is composed of the liquid diffusion coefficient D_L and an amplitude and viscosity dependent mixing term D_L'' accounting for the movement of the liquid

$$(8) \quad D_L' = D_L + D_L''$$

D_L and D_L'' are considered to be additive, since they are probably independent.

D_L'' depends directly on the shaking amplitude and inversely on the liquid viscosity. An estimation of the effective liquid layer thickness would require a determination of D_L'' . A measurement of the equilibration time and D_L for various substances in the same liquid is probably difficult to use for this purpose, because $D_L \ll D_L''$. It might be possible to estimate D_L'' by the measurement of the spreading of a nonvolatile substance in a tube, because in this case the contribution of d_L^2/D_L to the equilibration rate will be small. The conditions for this measurement should be such that the effective liquid layer thickness is the same as during operating conditions because d_L' and D_L'' probably are interdependent. This is concluded from the facts that the liquid in the tube foams during operation, and that the mechanical behaviour of a foam usually is different from that of a liquid.

From a preliminary experiment in which a gaseous hydrocarbon sample was injected into a tube containing 1 cm³ of paraffin oil and vibrated without changing the gas phase in the tube, the equilibration time at 0.7 mm amplitude was found to be about 1/3 min, while for the same tube at rest the time was about 1/2 h. The shaking, which caused a reduction in equilibration time by a factor of 100, thus allows a gas velocity of $(1/t_e) \cdot V_g/\text{tube}$, or $3 \cdot 14 = 42$ cm³/min before H becomes > 1 . In a distribution experiment with paraffin oil, the value 50–75 cm³/min was found for U_{\max} . In a similar experiment with cineole, U_{\max} was found to be about 600 cm³/min (Fig. 11). About the same value was obtained on determination of the distribution coefficient of cyclohexane on quinoline at various gas flow rates by logarithmic dilution (Fig. 8); when the equilibration is insufficient, the solute lags behind in the liquid, the values obtained for k being then too high. In Fig. 9, the relation between U_{\max} and the solvent viscosity is illustrated. A plot of $\log U_{\max}$ against $\eta^{1/2}$ gives an approximately straight line, indicating the empirical relationship $\log U_{\max} = 3.2 - 0.11 \cdot \eta^{1/2}$ (Fig. 9)

at 0.7 mm amplitude, or, if $U_{\max} = V_g \cdot \frac{1}{t_e}$,

$$(9) \quad \log t_e = \log V_g - 3.2 + 0.108 \cdot \eta^{1/2}$$

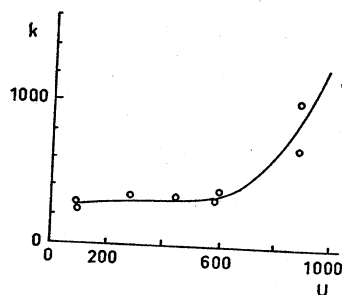


Fig. 8. Influence of the carrier gas velocity on the determination of the distribution coefficient. Solute cyclohexane, solvent quinoline.

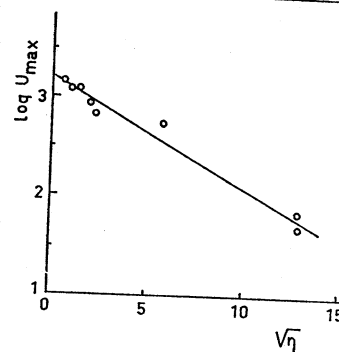


Fig. 9. $U_{\max} = f(\eta)$.

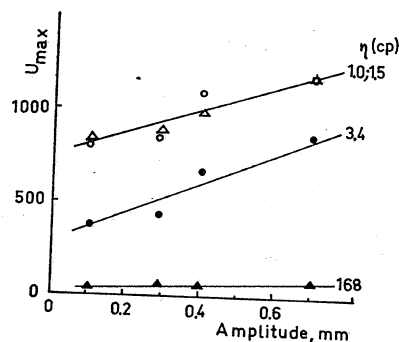


Fig. 10. $U_{\max} = f(\text{Ampl.})$ with η as parameter.

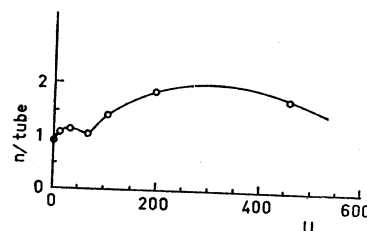


Fig. 11. Dependence of number of plates/tube on gas (N_2) flow rate. Solute benzene. Stationary phase cineole. $V_L = 0.5$ cm^3/tube . Room temp. Sample size: 0.5 cm^3 liquid.

t_e , min; η , CP. From Fig. 10 it is seen that at constant viscosity, U_{\max} is approximately a linear function of the amplitude. At a low viscosity and zero amplitude U_{\max} has an appreciable value (about $500 \text{ cm}^3/\text{min}$ for heptane, $\eta = 0.42$), a fact that indicates the mixing action of the gas bubbling through. U_{\max} is somewhat higher at larger liquid volumes (Table 3), in accordance with eq. (9).

Because, for a tube efficiency of at least 1, the range of gas velocity is wide when the liquid viscosity $< 30 \text{ CP}$, the pressure drop or length of train will be no problem. The power of the vibrator must, of course, be increased for larger tube numbers. The maximum allowable inlet to outlet pressure ratio is

$$(10) \quad \frac{P_i}{P_o} = \frac{U_{\max}}{U_{\min}}$$

Table 3

 U_{\max} at various liquid loads. Amplitude 0.1 mm.

V_L cm ³	U_{\max} cm ³ /min	V_L	U_{\max}
1	600	4	800
2	600	6	700

2. H -gas velocity curves

Between U_{\max} and U_{\min} , as defined in the previous section, the efficiency was higher than one plate per tube (Fig. 11). From the plots of H against gas flow rate (Fig. 12 a—e) it is seen that each tube acts as a short chromatographic column, the additional plates probably being formed by the wetted walls of the tube and by the foam present in the tube at the higher gas velocities. In the $H-U$ curves at an intermediate velocity there is a maximum which was at first thought to be due to experimental error. It was repeatedly obtained, however, despite changes in solvents and amplitudes. The U -value at which it occurs seems to be independent of the amplitude but tends to be lower at a higher viscosity (Table 4). At the viscosities of 1.07 and 1.5 CP it is pronounced. Its position changes from 150 to about 100 cm³/min when the liquid volume is increased from 2 to 6 cm³/tube ($\eta = 1.5$).

Table 4

Position of the H maximum on the $H-U$ curves at various amplitudes.

η CP	U cm ³ /min	η	U
1.07	200	4.4	70
1.5	150	33	100
3.4	75	168	30

3. Dependence of H on viscosity and amplitude

The amplitude of shaking and the viscosity of the liquid phase together determine the efficiency of mixing of the phases. Additionally, the flow of carrier gas has a mixing action.

As is seen from Fig. 12, the optimum gas velocity is shifted towards higher U -values by increasing amplitudes. This shift, which is explained by the lower resistance to mass transfer (shorter equilibration

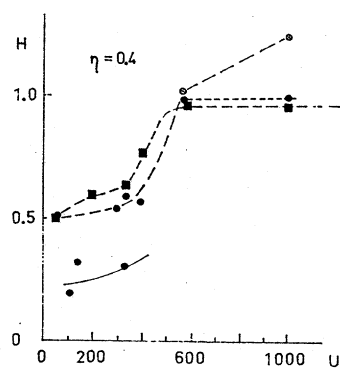


Fig. 12 a.

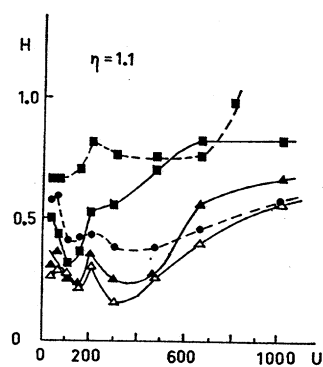


Fig. 12 b.

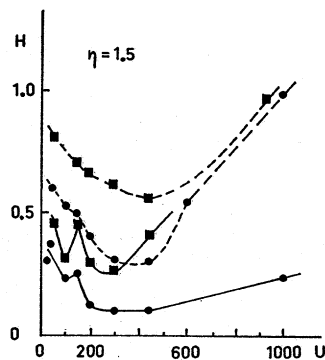


Fig. 12 c.

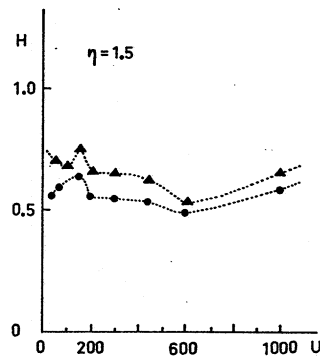


Fig. 12 d.

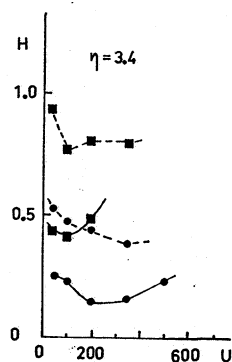


Fig. 12 e.

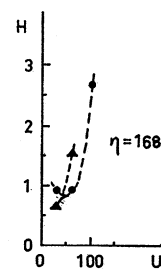


Fig. 12 f.

Fig. 12 a-f. Relation between plate height and gas flow rate at various amplitudes of shaking and with stationary phases of different viscosities.

Solid lines: components with $k = 15$
 Broken » » » $k = 40-50$
 Dotted » » » $k = 150$
 Amplitudes ● 0.6 mm
 ■ 0.1 »
 ▲ 0.3 »
 △ 0.4 »
 ⊗ 0.0 »

time) and the increased spreading due to mixing, is more pronounced when liquids with higher viscosities are used.

With heptane as the liquid phase the $H - U$ curves are almost identical for different amplitudes. Between $U = 400$ and $600 \text{ cm}^3/\text{min}$, H rises rapidly to one and remains there until $U > 1000$. This might be regarded as an indication of the mixing action of the carrier gas. At the low viscosity of heptane, the mixing causes the solute to spread over the whole length of the tube even at high velocities. The existence of a balance between the reduction of resistance to mass transfer and the broadening due to mixing is clearly seen from Fig. 13 for the low gas flow rates. At the higher gas velocities the resistance to mass transfer becomes predominant, the H -amplitude relationship approaching linear form with increasing steepness.

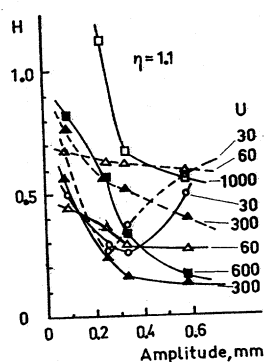


Fig. 13 a.

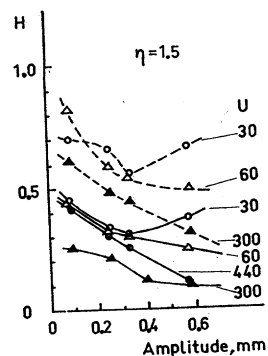


Fig. 13 b.

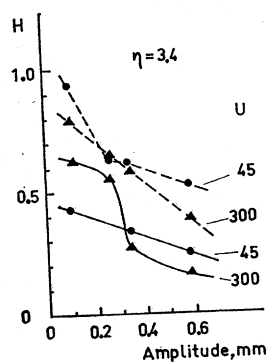


Fig. 13 c.

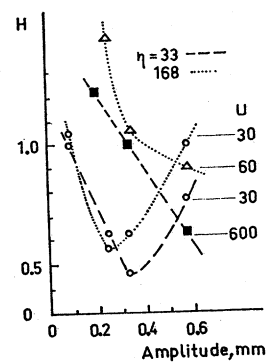


Fig. 13 d.

Fig. 13 a-d. Dependence of plate height on shaking amplitude (mixing), with U as parameter. Solid lines: components with $k \approx 15$. Broken lines: components with $k = 40-50$. Dotted lines: values for paraffin oil, $k = 60$.

4. Effect of the liquid volume

Plots of H against the ratio of liquid to gas volume are shown in Fig. 14 a and b. Similar changes in the slope were observed when measurements were made on cineole at $V_L = 0.5, 1$, and 2 cm^3 , where the change in the direction of slope occurred at about $U = 70 \text{ cm}^3/\text{min}$. The slope at low U was somewhat larger than for Shell Sol T .

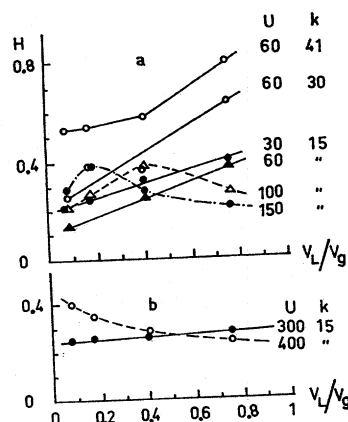


Fig. 14 a, b. Relation between H and liquid-to-gas volume ratio. Gas flow rate and distribution constant parameters.

5. Effect of the carrier gas diffusivity

A comparison of the variation of plate heights with U at different liquid volumes (Fig. 14) shows that the H -minimum is broader and extended to higher gas flow rates at higher V_L/V_g values than at low ones. This might partly be explained by a non-equilibrium in the lateral direction in the gas phase, exerting a broadening effect at low V_L/V_g .

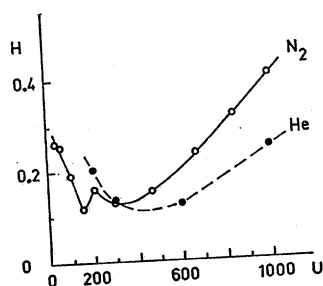


Fig. 15. Relation of plate height to gas velocity for two different carrier gases. A flow rate of $600 \text{ cm}^3/\text{min}$ corresponds to a velocity of 10 cm/sec .

With helium as the carrier gas, the optimum velocity is higher than with nitrogen (Fig. 15), showing that slow diffusion in the gas phase to some extent limits the efficiency in the upper half of the usable gas velocity range (if the liquid viscosity is not too high). At $k > 40$, the $H - U$ curves for He are almost identical with those for N_2 .

6. Effect of the distribution coefficient

The H -gas flow rate curves start from about the same value at U_{\min} (complete equilibration within the whole tube) and converge towards U_{\max} . The difference in H value for different distribution coefficients is greatest at the optimum gas velocity. Components with lower k are able to «climb» up the wetted tube walls before they are mixed into the whole liquid volume. From Fig. 14 it is seen that the slope of the plate height *vs.* liquid volume curve at low gas velocity at first increases with k and then decreases again. The plate height is almost constant when the distribution coefficient rises above 40 (Fig. 16).

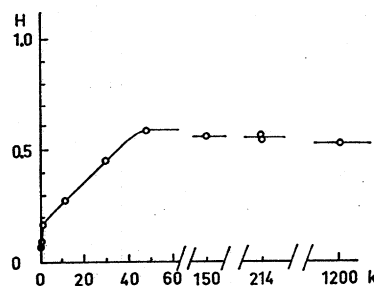


Fig. 16. The plate height for compounds with different distribution coefficients. Conditions: carrier gas He, $U = 200 \text{ cm}^3/\text{min}$. Amplitude: 0.1 mm. Solvent: Shell Sol T. $V_L = 2 \text{ cm}^3$. Compounds eluted.

7. Effect of the diameter of the inner tube

With increasing diameter of the inner tube a larger surface is provided, and the path for gaseous diffusion is shortened. At low gas velocities H is the same for different diameters. At an intermediate gas flow rate H shows an improvement, which is larger for substances with high distribution coefficients (Fig. 17). At liquid viscosities below 4 CP the improvement is small when the diameter exceeds 0.2 cm. At higher gas velocities the efficiency of tubes with 0.8 cm diameter inner tubes was lower than that of 0.4 cm tubes.

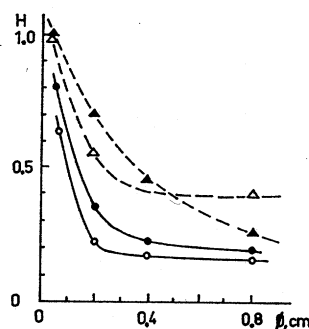


Fig. 17. Effect of inner tube \varnothing on efficiency.

- $k = 15, U = 120, \eta = 1.07$
 —●— $k = 15, U = 100, \eta = 4.4$
 - -△- - $k = 47, U = 120, \eta = 1.07$
 - -▲- - $k = 47, U = 100, \eta = 4.4$

8. Discussion of the results obtained with gas as the moving phase

Klinkenberg⁶¹ has shown that the broadening of a band caused by different factors is the sum of the effects of the isolated factors, provided these are independent. van Deemter *et al.*¹⁷ developed the rate theory, spread being expressed by an equation including an «eddy» diffusion term, a term for molecular diffusion in the longitudinal direction in the gas phase, and another for resistance to mass transfer in the liquid phase, i.e. the non-equilibrium term. Additional terms have been added to the equation for *HETP* to account for gas phase non-equilibrium^{54, 57}, lateral diffusion^{45, 51, 57}, and interaction between different paths of flow in a packed column³⁰.

The relations between *HETP* and various parameters reported in the previous section will be discussed empirically, on the basis of the additivity principle⁵¹. The spread of the solute bands due to the mixing of the liquid phase will be considered in addition to the other effects. It is assumed that the expression for one tube will be of the form

$$(11) \quad H = A + \frac{B}{U'} + \frac{B'U'}{U'} + \frac{B''U'}{U'} + CU' + \frac{C'}{U'}$$

«Eddy» diffusion	Molecular diffusion	Resistance to mass transfer gas phase	Lateral diffusion gas phase	Resist. to mass transfer liquid	Mixing term liquid
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The A term: This was estimated graphically^{9, 34} from the intercepts of the asymptotes of the hyperbolic experimental $H - U$ and $H - 1/U$ curves with the H axis. The values obtained are presented in Table 5. The A values obtained from the tangents to the discontinuity in the $H - U$

Table 5

Contributions of the A term to the *HETP*.Lo: A values estimated from the $H-1/U$ plot.Hi: » » » » » $H-U$ » V_L = liquid phase volume, cm³. η = viscosity of the liquid phase,CP. k = distribution coefficient of solute.

V_L	η	k	Amplitude, mm.							
			0.09		0.25		0.33		0.58	
			A values							
			Hi	Lo	Hi	Lo	Hi	Lo	Hi	Lo
2	0.4	50					0.0	0.3		
2	1.05	15	0.3	0.3	0.0	0.1	0.0	0.0	0.0	0.0
2	1.05	47	0.6	0.6	0.5	0.6	0.3	0.4	0.2	0.2
2	1.5	15	0.0	0.2	0.0	0.1	0.0	0.1	0.0	0.0
2	1.5	47	-0.2	0.5	-0.2	0.4	-0.2	0.4	-0.2	0.3
2	3.4	15	0.1	0.3	0.0		0.0	0.1	0.0	0.1
2	3.4	41	0.6	0.7			0.3	0.5	0.0	0.3
2	33	40							0.1	0.5
1	1.5	15	-0.1	0.1						
4	1.5	15	0.2	0.2						
6	1.5	15	0.1	0.1						
1	1.5	30	-0.5	0.1						
4	1.5	30	0.2	0.2						
6	1.5	30	0.1	0.2						

curves show a greater variation than the other values. In low viscosity liquids they show a tendency to be somewhat lower than the A values obtained from the $H-1/U$ curves. For liquids of low viscosity ($\eta = 0.42$ and 1.0, but not from $\eta = 1.5$ upwards) the $H-U$ curve is concave towards the U axis at high flow rates, especially at the lower shaking amplitudes, and generally concave towards the $1/U$ axis at low gas flow rates. As the tangent to the curve should intercept the H axis near the value of A , it is probable that A increases towards the lowest and highest flow rates, and is thus dependent on U . At velocities below the optimum gas flow rate A (the values from the $H-1/U$ curves) is larger than at gas flow rates above H_{\min} .

From experiments with packed columns, Bohemen and Purnell⁹ and also Giddings³⁴ conclude that the A term of the van Deemter equation is very low or zero and cannot usually be accounted for by eddies in the gas flow. Giddings, who has discussed the A term thoroughly³⁴, has shown that the effects of eddy diffusion are negligible below a certain gas velocity, estimated as about 10 to 100 cm/sec. According to his coupling theory²⁹,

A should increase with the flow rate, though experimental proof of this dependence is still lacking. In the Golay equation for open tubular columns there is no A term, in accordance with the low Reynolds number for open capillaries³⁵.

Comparisons between the effects observed in the shaking apparatus described and those in packed or open capillary columns should be made with caution, partly because the tubes are quite short and their connections narrow. The Reynolds number at a flow rate of 1000 cm³/min (16 cm/sec) is here about 50, if the asymmetry at the top of the tubes and the movement of the liquid are neglected, a value which is regarded as too low for turbulent flow to occur, except in packed media³⁴. The decrease of A with U at the lower and intermediate flow rates, together with its dependence on the distribution coefficient and the mixing amplitude (Table 5), suggests that A in the system described in some way might be connected with the liquid phase. A mechanism that would conform with the data presented is the asymmetric distribution of the liquid phase. If A had this meaning, its value should fall with rising U , show no appreciable variation with liquid volume, and have a minimum at a rather low viscosity, because at a very low viscosity the liquid will «reflux» more easily towards the bottom of the tube, whereas for a high-viscosity liquid a stronger gas flow and shaking amplitude is needed to bring about distribution of the liquid phase along the tube.

B terms: For the molecular diffusion term (B) in open tubular columns the value is $2D_g/U$ ^{35, 73}. According to the van Deemter equation, a change of carrier gas should affect only the B term, and $H_2 - H_1 = \frac{1}{U} (B_2 - B_1)$, if H_2 and H_1 are the plate heights obtained with two different carrier gases. Bohemen and Purnell⁹ found that a plot of the difference in H with carrier gases of different diffusivity against $1/U$ for a packed column is

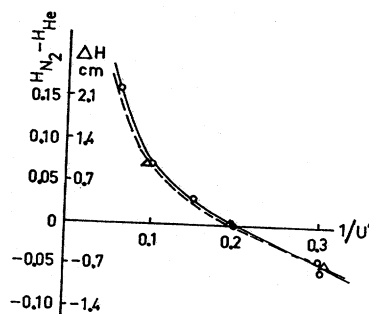


Fig. 18. Solid line: experimental curve. Broken line: calculated curve.
For explanations see text.

in fact curved. A similar plot of the values presented in Fig. 15 gives a curve which intercepts the $1/U$ axis (Fig. 18). This shows that the B term is not the only one to be affected by the carrier gas diffusivity. Taking the other B terms into consideration, the expression for the difference in *HETP* with different carrier gases becomes

$$(12) \quad H_2 - H_1 = \frac{1}{U'} (B_2 - B_1) + U'(B'_2 - B'_1 + B''_2 - B''_1)$$

Jones⁵¹ has given the expressions $k'^2 \cdot d_g^2 / (1 + k')^2 \cdot D_g$, where d_g is the gas film thickness, and (a numerical coefficient) $\cdot d_p^2 / D_g$, where d_p is the particle \emptyset , for the resistance to mass transfer in the gas phase, and the velocity distribution in the gas phase, respectively. According to Giddings³⁴ and also to Klinkenberg and Sjenitzer⁶¹, the spreading due to velocity differences and radial molecular diffusion are interdependent. Thus a correlation term should be added to the expression for *HETP* (eq. 11). This term might be of the form $2\varrho \cdot (B' \cdot B'')^{1/2} \cdot U$ ⁵¹. If, however, B' is very small, the correlation term disappears. In the shaking apparatus described, B' is probably small owing to the continuous movement of the liquid. For the velocity distribution term (B''), d_p has in this case to be substituted by the difference between the diameters of the outer and inner tubes. Neglecting B' , eq. (12) would here take the form

$$(13) \quad a \cdot U' \cdot \left(\frac{1}{D_{N_2}} - \frac{1}{D_{He}} \right) + \frac{b'}{U'} \cdot (D_{N_2} - D_{He})$$

The hyperbola obtained by substituting the values 0.137 and 0.363 cm²/sec for the diffusion constants of propane in nitrogen and in helium, and the empirical values 0.0286 and 14.17 for the numerical constants a and b' , fits the experimental results (Fig. 18).

The C term: For packed and open tubular columns the resistance to mass transfer in the liquid phase is^{17, 35, 51}

$$(14) \quad H_c = \frac{C'_L \cdot k'}{(1 + k')^2} \cdot \frac{d_L^2 \cdot U'}{D_L}$$

where C'_L = numerical constant.

It seems reasonable to assume that the C term for the apparatus in question would be of the same form as this expression, because the only difference regarding H_c introduced with the mixing is in the effective diffusion time. In equation (14), $C'_L \cdot d_L^2 / D_L$ is the time required by the molecule to diffuse to and from the gas-liquid interphase⁵¹. Here, this part of H_c should be obtained from expressions (7) and (8), see also eq. (9).

The C' term describes the broadening in the liquid phase. In packed and open tubular columns the effect of diffusion in the liquid phase is negligible; with the introduction of mixing, however, this term must be taken into account. An expression for the plate height contribution of C' may be derived by the simplified method of Jones⁵¹ for the treatment of broadening effects in solute transport systems. The time t for a molecule to move a distance l by diffusion is

$$(15) \quad t = \frac{l^2}{2D_L n'}$$

where D_L is the diffusion constant and n' the number of directions of interest. For this case, $\sigma^2 = l^2$ over a tube length L , n' is = 1, and $H = \sigma^2/L$, where σ^2 is the variance of the resulting solute band⁵¹. If it is assumed that the spread due to mixing is random, D is composed of $D_L + D_L''$, where D_L'' is the mixing constant, or

$$(16) \quad t = \frac{l^2}{2(D_L + D_L'')}$$

The time (t_L) spent by the solute in the liquid phase is the difference between the retention time and the time spent in the gas phase

$$(17) \quad t_L = \frac{L \cdot k \cdot V_L}{U' \cdot V_g}$$

Equalization of t and t_L and rearrangement gives

$$(18) \quad \frac{l^2}{L} = \frac{\sigma^2}{L} = H_C = \frac{2(D_L + D_L'') \cdot k \cdot V_L}{U' \cdot V_g}$$

The plate height should thus increase linearly with increasing V_L/V_g . This is seen to be true at low gas velocities (Fig. 14). These curves contain the effects of the other terms, these probably being rather small, however, compared with the C' term at low U . The gas bubbling through the liquid probably increases the mixing; this should lead to a steeper slope of the H vs. V_L/V_g curve at higher U ; this is counteracted by the fact that $H_C = f(1/U)$. It is seen from Fig. 14 that the slope is somewhat higher at $U = 60$ than at $U = 30$ cm³/min. When the gas velocity increases above 100–150 cm³/min, the slope at first decreases and then becomes negative, showing that the mechanism of mixing is here changed because the effect can only partly be explained by the inverse dependence of H_C on U and the reduction of the resistance to mass transfer in the gas and liquid phases. It is concluded that D_L'' should be composed of one term (mixing-amplitude) independent of gas flow rate, and another term dependent on gas flow rate.

At first, when $U \geq 100-150$, liquid sprays onto the walls of the tube, but refluxes according to its density and viscosity; then, at $U > 200$, the stream of gas prevents the liquid from refluxing, and the plate height falls. This view is supported by visual observation of the tube contents at various gas velocities. The discontinuity observed in the $H-U$ curves might be connected with this change in mechanism. Increasing film thickness in packed and in open tubular columns²⁰ causes H to rise more rapidly on the high velocity side of the optimum, and increases H_{opt} . That the plate height is not considerably increased at the higher flow rates with high V_L/V_g ratios in the shaking apparatus shows that the liquid mixing is not very much impeded by increasing the liquid volume, and that the foam produced in the tube forms some kind of obstacle in the longitudinal direction which tends to prevent the C' term from covering the whole tube length. H should increase with the distribution coefficient, in accordance with the experimental results obtained for compounds with a k value between 0 and 50. That H_{opt} does not increase above about 0.6 when k increases above 50 might be attributed to the tube geometry, the tube consisting of two concentric vessels.

II. LIQUID AS THE MOVING PHASE

1. Effect of a volume gradient on band shape

The reversed phase experiments were carried out without adjustment of the pressure gradient, and hence the ratio of gas to liquid volume increased in the direction of flow. The effective volume (v_p) of tube No. p , with the total volume V , was therefore

$$(19) \quad v_p = k \cdot V + \frac{m'RT}{(n-p) \cdot \Delta P + P_0} \cdot (1-k)$$

(m' = number of moles of stationary gas, ΔP the pressure drop across one tube and n = total number of tubes).

If the distribution coefficient = 1, $v_p = V$. The effective plate volume increases in the direction of flow if $k < 1$, and decreases if $k > 1$. Because the change in concentration in plate p per volume element of the moving phase is inversely proportional to the effective plate volume, the volume gradient leads to sharper solute bands for increasing v_p and broader bands for decreasing v_p , and the efficiency, or number of plates, cannot be measured in the usual way. Only for $k = 1$ is v_p constant; the plate number may then be calculated in the usual way. The v_p gradient will depend upon the flow rate, the viscosity of the liquid, and the geometry of the apparatus.

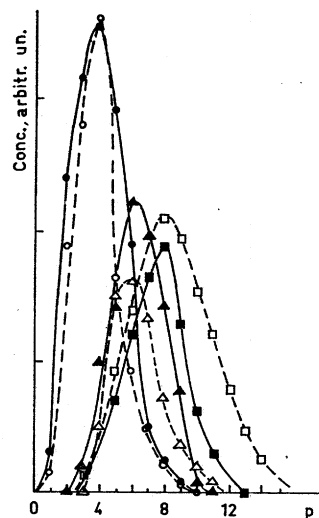


Fig. 19. The concentration is given in arbitrary units. \square \blacksquare propane, Δ \blacktriangle *i*-butene, \circ \bullet *n*-butane. Solid lines: liquid volume per tube constant (4.2). Broken lines: liquid volume decreases with tube number, from 5.0 cm³ in the first tube (No. 0) to 3.0 cm³ in tube No. 11. Mobile phase 40% *i*-propanol in water, $U_L = 3$ cm³/min. Distribution coefficients calculated from expt. in absence of vol. gradient: 0.725 (propane), 1.1 (*i*-butene), 1.85 (*n*-butane).

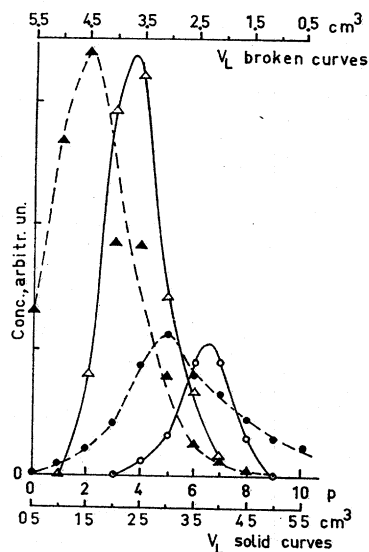


Fig. 20. Shape of the distribution curve in a volume gradient. Mobile phase N₂, stationary phase Sell Sol T. $U = 63$. Room temp. \circ \bullet propane, $k = 15$, Δ \blacktriangle *i*-butane, $k = 42$. Ampl. = 0.6 mm.

Distributions at constant liquid volume and in a volume gradient are illustrated in Fig. 19. The resolution is higher for the volume gradient. As a control, an experiment was made with gas as the moving phase, in both an increasing and a decreasing v_p gradient (Fig. 20). Again, the resolution measured is seen to be higher for increasing v_p , while the percentage impurity calculated from the surfaces is about the same.

2. Dependence of separation on liquid flow rate

The measure of efficiency chosen was the percentage impurity of two specified components after travelling equal distances. The separation factor of *iso*-butene and *trans*-2-butene was the same (~ 1.8) for the solvents used in this experiment, while the distribution coefficients for *iso*-butene were 6.5 (H_2O), 9.5 (H_2O -starch), and 1.1 (H_2O -*isopropanol*). The liquid volume varied almost linearly from 3.2 cm^3 in tube 0 to 0.3 cm^3 in tube 9 for water with a flow rate of 3 cm^3/min . The useful velocity range is from 1 to about 10 cm^3/min . The maximum velocity falls by about ten per cent as the viscosity increases from 1 to 4.9 CP (Fig. 21 a). The »reversed phase» $H - U_L$ curve for *iso*-butene in aqueous *isopropanol* solution is given for comparison (Fig. 21 b). The highest efficiency is seen to be of the order of three plates per tube (water).

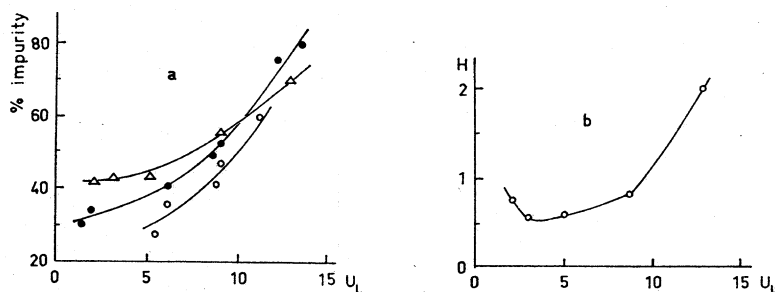


Fig. 21 a. Separation of propane and *i*-butene, expressed as % impurity, when the maximum of the propane is in tube No. 8. Mobile phases: ● 8% starch in water, $\beta = 4.85$ CP; ○ water, $\eta = 1$ CP; Δ 40% *i*-propanol in water, $\eta = 2.85$ CP. Stationary phase air. Amplitude of mixing 0.3 mm. Room temp. — b. Approximate plate height for *i*-butene (calc. from eq. 1, 2) in 40% aqueous *i*-propanol.

For the efficient use of a distribution apparatus, the question of resolution must be considered. If the maxima of the solute bands 1 and 2 are in tubes p_1 and p_2 , a separation factor α^x may be defined as (from eq. 3)

$$(20) \quad \alpha^x = \frac{p_1}{p_2} = \frac{V_g/V_L + k_2}{V_g/V_L + k_1}$$

If we put $n_1 - n_2 = b \sqrt{n_2}$ or $b \cdot \sqrt{n_1}$, where b is the number of standard deviations that separates the two maxima from each other, and eliminate n_1 and n_2 successively with the aid of (20), the number N of plates required for a separation becomes^{93, 94}

$$(21) \quad N = \sqrt{n_1 n_2} = \frac{b^2}{\alpha^x + \left(\frac{1}{\alpha^x}\right) - 2}$$

If $k_1 = 7.25$, $k_2 = 20$, $n_1 = 100$, and $n_2 = 49$, the solute maxima are separated by six standard deviations ($b = 6$), because $3 \sqrt{n_1} = 30$ and $3 \sqrt{n_2} = 21$ according to the plate theory^{54, 67}. The minimum between the solute maxima is at $n = 70$. If $V_g/V_L = 5$, $\alpha^x = 2.04$. Equation (21) gives $N = 68$, or two plates below the number required.

In 1941, Martin and Synge⁶⁷ derived the expression relating V_g/V_L , k_1 and k_2 and N for $b = 6 (M)$, which on rearrangement gives

$$(22) \quad N = \left(\frac{3 + 3\alpha^x}{\alpha^x - 1} \right)^2$$

or for the above example, $N = 77$. The formula of Scott and Hazeldean⁸⁷ here gives $N = 78$. The discrepancy between (21) and (22) diminishes with increasing N . Other expressions for N ^{6, 11, 16, 18, 75} give values ranging from 22 to 130 for the above example, owing to approximations made in deriving them.

Equation (21) may be taken as empirical indication that the minimum between two solutes is at the geometric rather than the arithmetic mean of the peak maxima positions. The resolution is defined as the distance between the peak maxima divided by the arithmetic mean of the peak widths². The above considerations indicate that for low N values the denominator should be the geometric mean.

Equation (21) holds for the case in which the plate height for components 1 and 2 is equal.

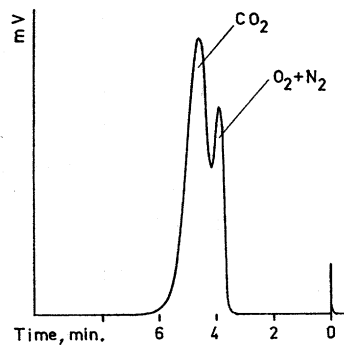


Fig. 22. Elution of a mixture of CO_2 and air. Conditions: 57 tubes, ampl. 0.1 mm, $V_L = 2 \text{ cm}^3$ Shell Sol T /tube, $U = 200 \text{ cm}^3$ He/min. Sample size 5 cm^3 .

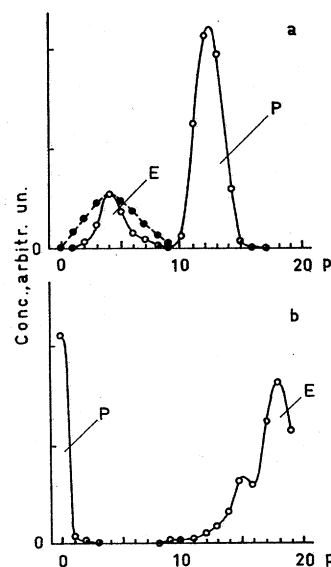


Fig. 23. Separation of ether (E) and n -pentane (P). Ordinate: amount of substance/tube, arbitrary units. Abscissa: tube number. Total amount of mixture: 20 mg. Room temperature. a) Mobile phase: nitrogen, flow rate $32.5 \text{ cm}^3/\text{min}$. Stationary phase: water, $1 \text{ cm}^3/\text{tube}$. Time: 5.5 min. \circ Experimental values. \bullet Calculated Poisson distribution assuming 1 plate/tube. b) Mobile phase: water, average flow rate $2 \text{ cm}^3/\text{min}$. Time: 24 min. Average amount of water/tube: 1 ml. Stationary phase: air.

From (20) it is seen that the separation of compounds with low distribution coefficients is improved by the use of large stationary to moving phase ratio. Thus CO_2 and N_2 , which are usually regarded as inert compounds on gas chromatographic columns (V_g/V_L 25 – 500), are separated on a hydrocarbon solvent if $V_g/V_L = 7$ (Fig. 22).

For low values of the distribution coefficients, the advantage of reversed phase distribution is also obvious. From the experiment illustrated in Fig. 23 a (stationary phase water) the following values are obtained:

$V_R = 175 \text{ cm}^3$, $k_{\text{pentane}} = 0.45$, $k_{\text{ether}} = 22.4$, $\alpha_{\text{exp}}^* = 2.70$, α^* from (20) is 2.69. With water as the moving phase (Fig. 23 b): $k_{\text{pentane}} = 1/0.45 = 2.22$, $k_{\text{ether}} = 1/22.4 = 0.045$, $\alpha_{\text{exp}}^* = 19$, α^* from (20) = 18.4.

2. Preparative separation

10 cm³ of benzene-cyclohexane mixture (1:1) was quantitatively separated, using 5 cm³ of quinoline/tube, a carrier gas flow of 100 cm³/min, and twenty tubes in an overnight run with a tube efficiency slightly greater than one.

The elution curve obtained on injection of 20 g of ethyl ether-methyl formate mixture (1:1) is shown in Fig. 24. The conditions were: $V_L = 5 \text{ cm}^3$ Shell Sol T/tube, inner tube $\varnothing = 2 \text{ mm}$, 20 tubes, $U = 1000 \text{ cm}^3 \text{ N}_2/\text{min}$, room temperature. Both components were eluted in 38 min, the tube efficiency being one. This represents the upper limit of the throughput in amount of material separated per unit time, with an apparatus of the dimensions given.

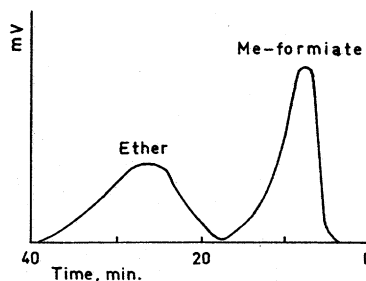


Fig. 24. Elution curve of the preparative separation of ether and methyl formate.

As an example of trace separation, the concentration of volatile components from milk, in which the large amount of water disturbs gas chromatography, is given. 20 cm³ of milk was injected into the apparatus, $V_L = 2 \text{ cm}^3$ Shell Sol T/tube, $U = 60 \text{ cm}^3 \text{ N}_2/\text{min}$, during 1 h at room temperature. The contents of tubes Nos. 5 to 15 were distilled in a high vacuum at room temperature and the distillate ($\sim 20 \mu\text{l}$ consisting partly of solvent) injected into a gas chromatograph. A concentration factor of about 100 times the amount of volatiles in 10 cm³ of head space vapour of milk at room temperature was obtained.

3. Gradient development

With gas as the stationary phase, the use of a liquid concentration gradient for the elution of slowly moving components or improvement of resolution is possible. Fig. 25 a illustrates a gradient development of a hydrocarbon mixture, in which the moving phase is at first pure water, 450 cm³ effluent, then water with linearly increasing acetone concentration. At the end of the experiment, the acetone concentration fed was 29%. The linear gradient was achieved by the method of Bock and Ling⁸. As a matter of interest, the resolution of *n*-butane and *i*-butene may be compared with that obtained on a 4 m dinonylphthalate conventional gas chromatography column (Fig. 25 b).

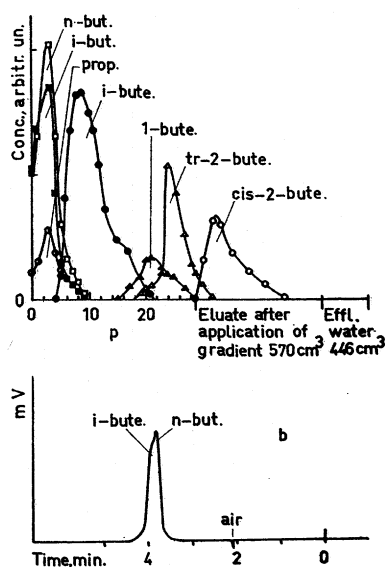


Fig. 25 a. Gradient development. $U_{\text{liq.}} = 7.3 \text{ cm}^3/\text{min}$, $V_{\text{Lav.}} = 2. \text{ cm}^3$, Room temp., Ampl. = 0.3 mm, Time = 3.25 h. — b. Gas chromatogram, column 10% dinonylphthalate on 60–80 M chromosorb, 4 m, \varnothing 4 mm, Room temp., $U = 60 \text{ cm}^3/\text{min}$.

4. Use of the whole number of tubes

A component may be run in a distribution apparatus until its width is equal to the number of stages, in the following ways:

- a. Employing two columns or trains and letting the component circulate between these⁶⁶. Half the length of the apparatus is here used to its total capacity.

b. Running the component back and forth, moving the phases alternately⁴², or using a continuous countercurrent stream, as in column distillation.

c. Circulating the moving phase continuously in one direction⁷⁴.

In the case of method *b*, it must be remembered that with the apparatus described here, the maximum number of plates/tube in reversed phase operation is less than when the gas is used as the moving phase. Thus method *c* gives a higher total plate number here. Also, the spread of a solute is greater if the effective plate volume decreases in the direction of flow. Therefore the temperature should be alternately raised and lowered to keep the distribution coefficient > 1 .

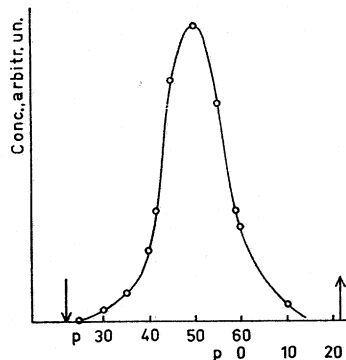


Fig. 26 a. Distribution curve of *n*-butane after recycling. Arrows indicate carrier gas inlet and outlet points at the end of the experiment.

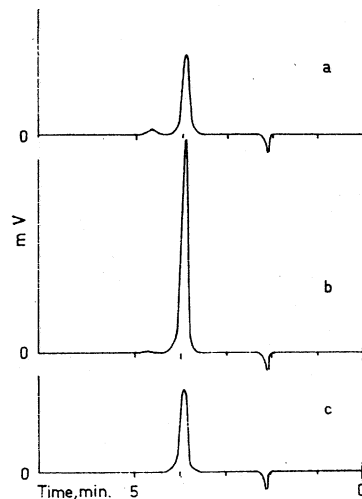


Fig. 26 b. Purity test of *n*-butane. a, b, and c from tubes 42, 50, and 59 in Fig. 26 a. For column conditions, see Fig. 3.

If method *c* is used in a discontinuous way so that the inlet point for the carrier gas is moved to the rear of the solute band when the front of the band is at the last tube, the distribution coefficient and the spread of the desired component must be known. The plate theory may then be applied in the following way. The solute is first run so that its front is in the last plate, P_t/H , where P_t is the number of tubes. Taking the band width as equal to four times the standard deviation, the rear is then in the plate

$$(23) \quad P_{F(0)}/H = \frac{P_t}{H} + 4 \left(1 - \sqrt{\frac{P_t}{H} + 1} \right)$$

Carrier gas is now let in at tube $P_{F(0)}$ while P_i is connected to the first tube until the front is in plate No. $P_{F(0)}/H$. It is seen that if the inlet point is changed m'' times, the inlet points may be successively calculated from

$$(24) \quad \frac{P_F(m'')}{H} = \frac{P_i}{H} + \frac{P_F(m'' - 1)}{H} + 4 \left(1 - \sqrt{\frac{P_i}{H} + \frac{P_F(m'' - 1)}{H} + 1} \right)$$

By this method *n*-butane was separated from 20 cm³ of a hydrocarbon mixture (Fig. 3). The distribution of the *n*-butane after 13 changes of the gas inlet point is shown in Fig. 26 a. The conditions were: room temperature, 1.5 cm³ Shell Sol *T*/tube, gas flow 60 cm³ N₂/min, 60 tubes, the efficiency for *n*-butane according to a preliminary experiment 4 plates/tube, amplitude of shaking 0.2 mm. In Fig. 26 b a purity test of the *n*-butane is shown. The spread of the butane gives an efficiency of about 6 plates/tube, probably because the band width was taken as $4 \cdot \sigma$ instead of $6 \cdot \sigma$ (24). The separation achieved corresponds to about 1650 plates.

For an apparatus with P_i/H plates the total number of plates attainable according to the plate theory is $\left(\frac{P_i}{4H}\right)^2$ if the compound is allowed to spread until four times its standard deviation is equal to the number of plates. When the inlet point for the moving phase has been changed 10 times, the number of plates used is $0.45 \cdot n_{\text{total}}$, after 20 times $0.63 \cdot n_{\text{total}}$, and after 30 times $0.75 \cdot n_{\text{total}}$. Therefore, the use of more than $\frac{1}{2} \cdot n_{\text{total}}$ is inconvenient without the use of a pump, which, of course, should be free from slip.

GENERAL DISCUSSION

This simple method of distribution in a series of washing flasks differs from other gas-liquid countercurrent methods in that the liquid phase is vigorously mixed, the stages are very short, and packing is absent. The system was originally intended for the prefractionation of complex, dilute solutions prior to analytical or milligram scale gas chromatography. For such a «cleaning up» system it is convenient to be able to calculate the position of a given component. For the separation of trace components from large amounts of solvent of similar volatility it is an advantage if elution is avoided, because of difficulties in condensation. In fact, the trace component is here transferred to a solvent of widely different volatility, and this solution may then be treated by vacuum manipulation, in which losses are small. The division into short stages obviates the necessity of eluting all the material, for slowly-moving components may be picked out anywhere. Thus operation at a low temperature to avoid artefact formation is made

easier. Because of the capillary connexions, the procedure may be halted intermittently for sampling without any broadening of the bands. The length of the apparatus and the effective plate volume may easily be adapted to suit the needs of the problem in question.

The liquid mass transfer resistance term is proportional to the square of the liquid layer thickness¹⁷. There are two ways by which a reduction of d_L may be brought about, — spreading over a large surface or mixing. The first of these is used in gas chromatography columns. In extractive distillation, the mixing due to eddies during the flow down the column is very slow. In spinning band columns the mixing chiefly affects the vapour phase. The use of mixing makes smaller cross-sectional dimensions possible, and as far as a preparative apparatus is concerned, programmed temperature should be more convenient here than in packed columns, because a radial temperature gradient is avoided (in packed columns, however, the radial temperature gradient could be reduced by dielectric heating or the use of a packing material of high heat conductivity, such as metal beads).

During the course of the work, some other features of the system became evident. These will be discussed below.

In preparative separation, a throughput of about 30 g of eluted material per h is possible without recycling. This is of the same order as in laboratory extractive distillation⁸², but considerably less than the throughput of large gas chromatography columns^{5, 86}. The throughput might possibly be increased by using elevated temperatures and more efficient mixing techniques.

The optimum plate heights observed are of the same order of magnitude as those in spinning band columns but are five times the plate height obtainable with large packed chromatography columns⁴⁵. Compared with gas chromatography columns, however, the length of apparatus allowable is larger because of the low pressure drop across the tubes. If a pressure drop of 2 atmospheres with atmospheric pressure at the outlet is allowed⁵⁴, the apparatus will have 10000 tubes. For a gas flow of 300 cm³/min at the outlet, the inlet velocity is then 100 cm³/min. It would thus not be too unrealistic to assume an average efficiency of 2 plates/tube provided the distribution coefficients are not higher than 15. On recycling, the maximum usable number of plates is then 25 million. Such a unit would require a battery of 100 vibromixers; its overall dimensions would be 3 · 5 · 2 metres and it could be used for the separation of isotopes or organic isomers.

The scaling-up of the plate-volume should be considered with more reservation. It seems possible, however, that each tube could be replaced by a tower equipped with a circulating pump and a spray nozzle at the top to bring about mixing, as in the industrial absorption vessels used for corrosive gases.

For optimalization of the separation process the specificity of the liquid phase, the temperature dependence of the liquid viscosity and the distribution coefficients have to be considered, together with the fact that the plate number of the apparatus increases with decreasing k . From Fig. 16 and equation 21 it is seen that for a gas to liquid ratio of 5 and a ratio of the distribution coefficients of 1.5, the optimum separation is obtained when the distribution coefficients have values of about 4 and 6. This is not very far from the value $k = 3$ given for optimum separation on chromatography in open tubular columns by Golay³⁷.

It may be mentioned that the apparatus described can also be used for liquid-liquid distribution. In a separation of 2-chloroethanol from its formate with water as the stationary, and pentane as the moving phase (10 cm³/min), a tube efficiency of 1.0 was found. The difference between tube efficiencies in liquid-liquid and gas-liquid systems is probably due to the slowness of diffusion in the liquid phase. A more rapid stirring of the liquid phases leads to emulsification.

Gas chromatography is useful as a rapid method for the study of solute-solvent interactions. As compared with the exact but time-consuming stationary vapour-liquid equilibrium methods, however, it is hampered by the possibility of adsorptive effects and the rather limited range of liquids usable. It is believed that the method presented here could be used to complement present procedures. When the differences in distribution coefficients are small, the use of the 1-tube apparatus for their determination is not enough. The difference in distribution coefficients should then be measured by partition with many tubes. When the absolute values of the distribution coefficients are small, they are best measured by reverse phase distribution.

SUMMARY

The use of a series of washing tubes, with mixing of the liquid phase, for preparative gas-liquid multiple distribution is described. The plate height per tube when gas is the moving phase has been studied in relation to the gas flow rate, the degree of mixing, and the distribution coefficients of the solutes. It is discussed in terms of the gas chromatography rate theory. Reversed phase gas-liquid distribution is described together with liquid-gradient development, and the dependence of efficiency upon liquid flow rate has been studied. Resolution is compared for normal and reversed phase distributions. A method has been developed for the rapid measurement of distribution coefficients. The distribution method is discussed in relation to extractive distillation and gas chromatography.

LIST OF SYMBOLS

A	= «eddy» diffusion term
a	= numerical constant
a_D	= thickness of vapour layer
B	= molecular diffusion term
B'	= resistance to mass transfer (gas phase) term
B''	= lateral diffusion (gas phase) term
b	= distance between the maxima of two solute bands in terms of the standard deviation of the bands
b'	= numerical constant
C	= resistance to mass transfer (liquid) term
C'	= «mixing» term
C_g	= concentration in gas phase
C_L	= concentration in liquid phase
C'_L	= numerical constant
D	= lateral diffusion term
D_D	= diffusion coefficient (vapour)
D_g	= diffusion coefficient (gas)
D_L	= diffusion coefficient (liquid)
D'_L	= «effective liquid diffusion coefficient»
D''_L	= «mixing coefficient»
d_L	= thickness of liquid layer
H	= height of one theoretical plate (tubes/plate)
H_C	= contribution of the C' term to H
H_D	= average vapour flow rate
$HETP$	= height of one theoretical plate (cm)
H_H	= vapour flow rate (moles/sec area of tube cross-section)
k	= distribution coefficient
k'	= amount of solute in liquid phase/amount of solute in gas phase
L	= length of one tube
l	= distance
m'	= moles of stationary gas/tube
m''	= number of changes of the inlet point for mobile phase
N	= number of theoretical plates necessary for a given separation
n	= number of theoretical plates; n_t = plate containing band maximum
n'	= number of directions
P	= pressure (atm). P_i = inlet pressure, P_o = outlet pressure
P_F	= tube containing the rear of a solute band ($2 \cdot \sigma$ behind maximum)
P_t	= total number of tubes in an apparatus
p	= tube number
p_o	= vapour pressure (pure compound)
p_t	= tube containing band maximum

R	= gas constant (1 atm/mole degree)
t	= time
t_e	= equilibration time (min)
U	= gas flow rate (cm ³ /min)
U'	= gas velocity (cm/sec)
U_L	= liquid flow rate (cm ³ /min)
V	= total volume of one tube
V_g	= gas volume/tube
V_g'	= gas volume/theoretical plate
V_L	= liquid volume/tube
V_L'	= liquid volume/theoretical plate
V_R	= retention volume
v_p	= effective volume of one tube
W	= amount of substance (moles or g)
W_t	= band width
w	= band width (theoretical plates)
α	= volatility ratio
α^x	= separation factor
α_e	= volatility ratio in presence of a third liquid component
β	= slope
γ	= activity coefficient
η	= viscosity of liquid phase (CP)
ϱ	= correlation factor
σ	= standard deviation of a solute band ($1/4 W_t$ or $1/4 w$)

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